

DOE – BATTERY 500 REVIEW - 2018

Status and Challenges of Electrode Materials for High Energy Cells

Presented by
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2018 DOE Vehicle Technologies Program Review

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Project ID #
bat359

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OVERVIEW

Timeline

- Project start date: 10-01-2016
- Project end date: 9-30-2021
- Percent complete: 30%

Budget

- Total project funding
 - DOE \$50M
 - Contractor share: Personnel
- Funding received
 - FY17: \$10M
 - FY18: \$10M

Barriers

- Barriers addressed
 - High energy density of 500 Wh/kg
 - Abuse-tolerant safer electrodes
 - Energy vs Safety
 - Cycle life

Partners

- Project Lead
 - PNNL
- National Laboratories
 - PNNL, INL, Brookhaven
- Academia
 - UC San Diego, U. Washington, U. Texas

RELEVANCE

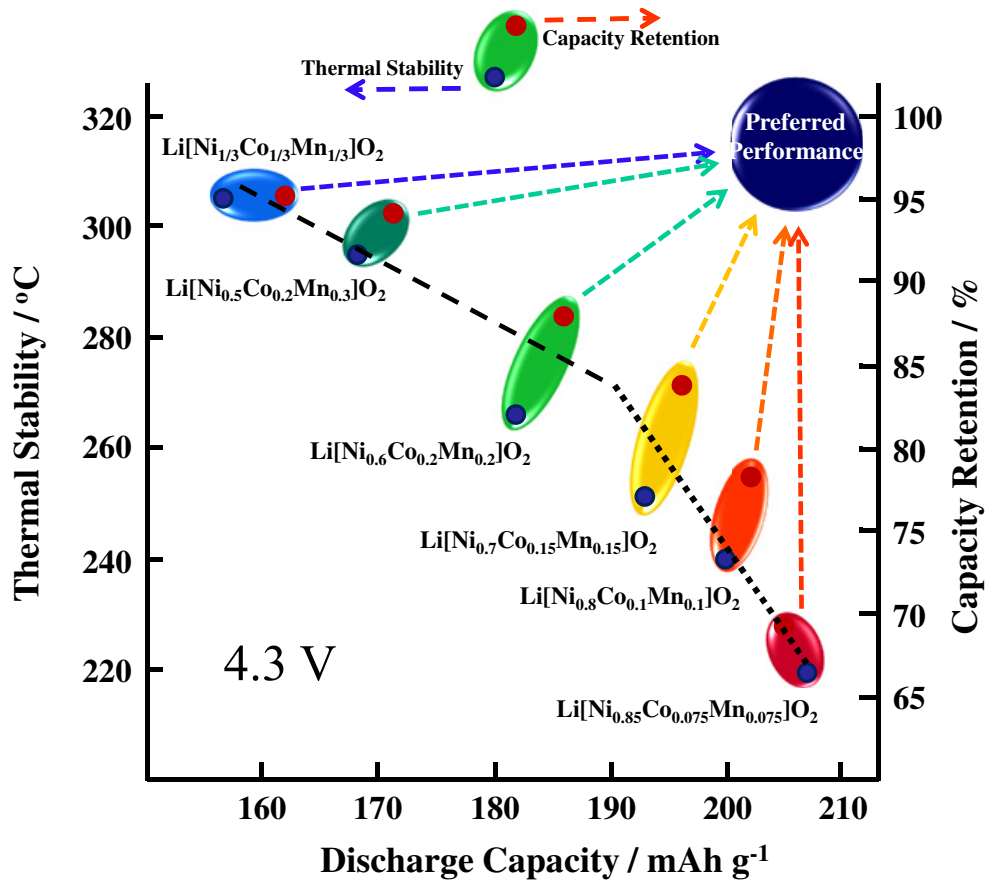
- **Overall Battery 500 Objective**
 - Develop commercially viable Li battery technologies with a cell level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable utilization of maximum capacity of advanced electrode materials
- **Chemistry**
 - Utilize a **Li metal anode** combined with a compatible electrolyte system, and either
 - A **nickel-rich NMC** or S
- **Keystone project (1): Materials and Interfaces**
 - Provides the materials and chemistry support for Keystone projects
 - (2) Electrode Architecture, and
 - (3) Cell Design and Integration

MILESTONES: KEYSTONE 1 and BINGHAMTON

| End date | 9/30/2017 | 12/31/2017 | 03/31/2018 | 06/30/2018 | 09/30/2018 |
|--|--|---|---|--|---|
| Type | Quarterly Q4 | Quarterly Q1 | Quarterly Q2 | Quarterly Q3 | Quarterly Q4 |
| Keystone Project 1 Materials Interfaces | Battery500 Annual: Demonstrate 1 Ah pouch cell with 300 Wh/kg energy density, and over 50 cycles Completed | Scale up the synthesis capacity of high Ni content NMC to 500 g Completed | Establish the stage II baseline coin cell performances using commercial high-Ni NMC at high loading in cathode, lean electrolyte and thin Li metal film anode (with the N/P ratio of ca. 2) Completed | Establish the new high-Ni NMC baseline material (Ni > 70%) and coin cell performance using the materials synthesized by the team and supplied by other sources Ongoing | Increase the cycle life of Li/high-Ni NMC cells using the materials synthesized by the team to 100 cycles (stage II coin cell protocol); Test new electrolyte Ongoing |
| Binghamton | Determine impact of cathode loading on capacity Completed | Provide the key electro-chemical data for the 622 and 811 NMC materials Completed | Recommend with Keystone 1 team the preferred NMC composition where $Ni \geq 0.7$, based on experimental and modeling studies Completed | Determine attributes of 811 vs NCA Ongoing | Develop a range of current collector options that will reduce their overall weight Ongoing |

CHALLENGES OF HIGH NICKEL LiMO₂

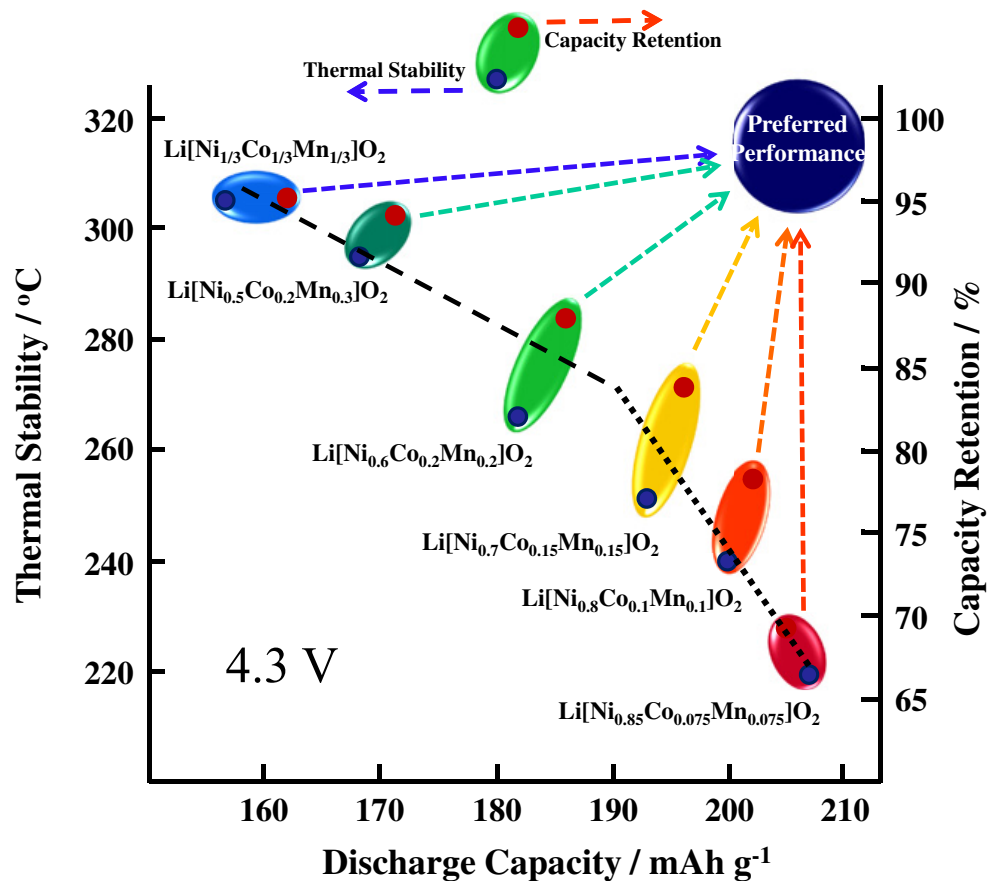
- Ni content drives the energy up, **but**
 - **Thermal stability decreases**
 - **Capacity retention decreases**



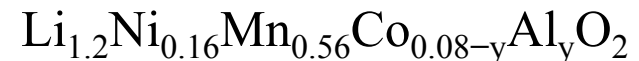
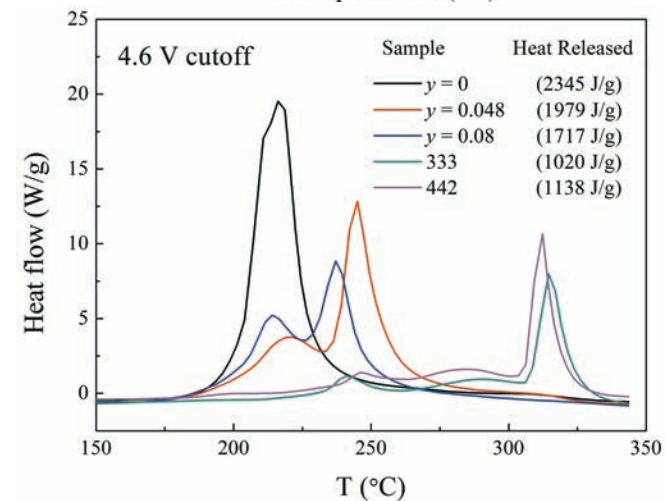
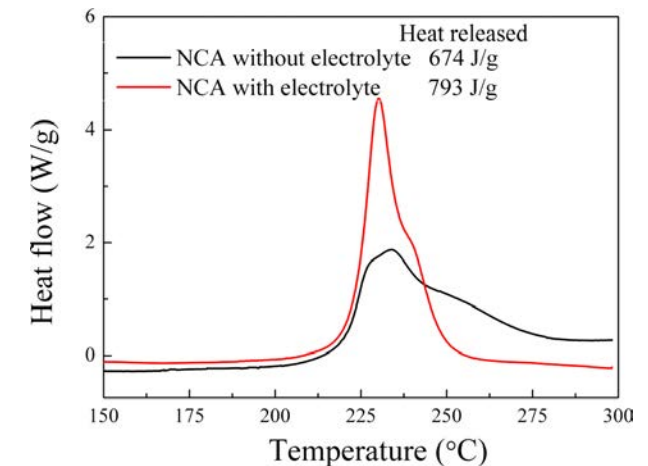
Noh et al, J. Power Sources, 233 (2013) 121-130.

CHALLENGES OF HIGH NICKEL LiMO₂

- Ni content drives the energy up, **but**
 - **Thermal stability decreases**
 - **Capacity retention decreases**
- Impact of Al on thermal stability
 - NCA low stability at 4.6 V
 - LiMn-rich stabilized by 5% Al



Noh et al, J. Power Sources, 233 (2013) 121-130.



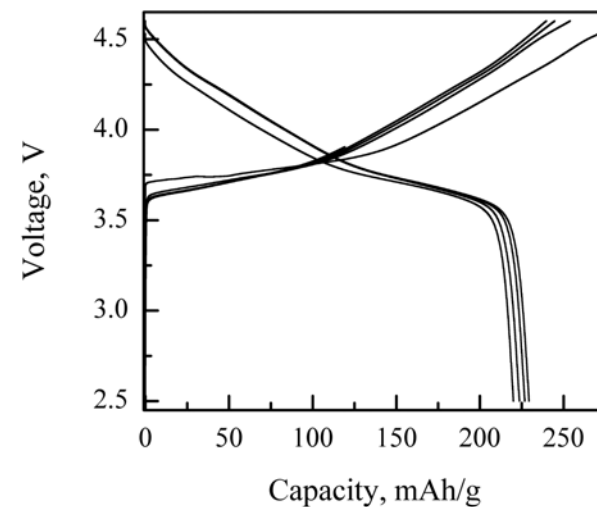
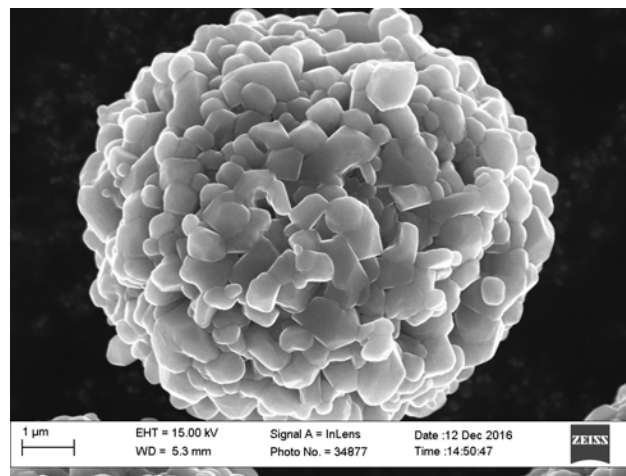
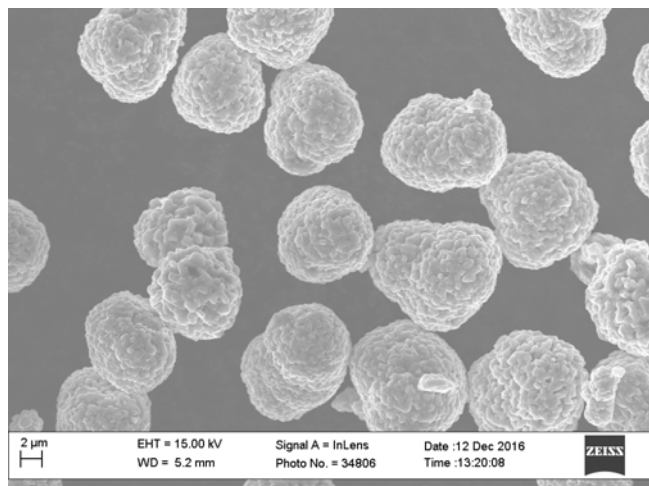
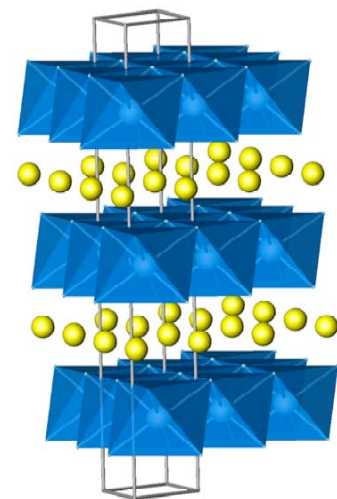
BATT: Whittingham et al, JECS, 159, A116 (2012)

KEYSTONE 1 APPROACH (to expedite progress)

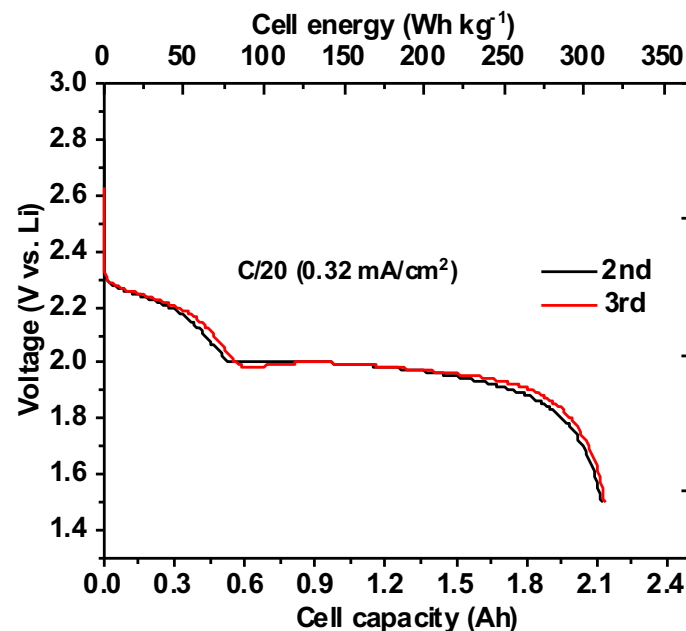
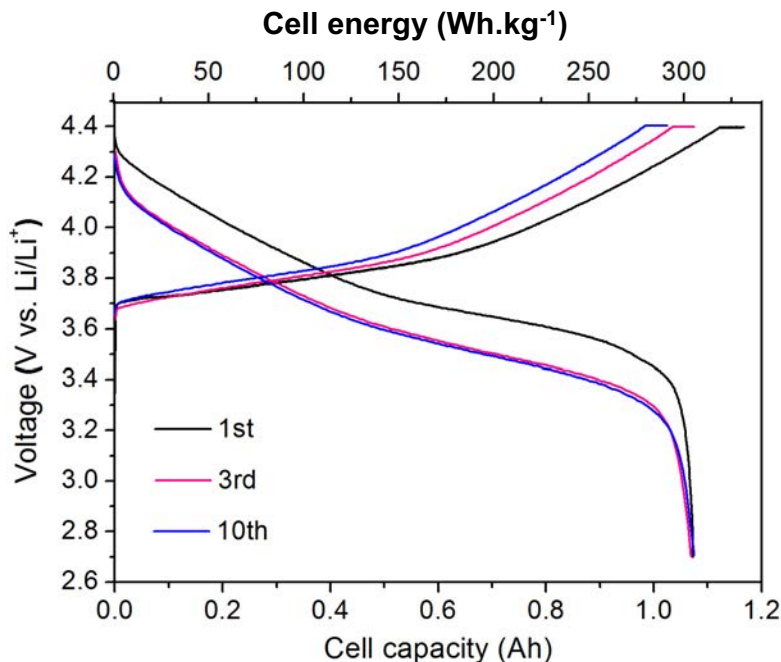
- Obtain commercial NMC materials as baseline NMC cathodes
 - 622 and 811 obtained indirectly from South Korea supplier (*BU/UCSD*)
 - NCA obtained from various sources (*BU/UCSD*)
 - Utilize knowledge from DOE NECCES study on model compound NCA (*BU/UCSD*)
- Evaluate NMC compositions, and make recommendations for future studies
 - Use **622** as baseline, against which materials will be compared
 - Use for consortium studies in initial years
 - Use to meet **Year 1 full cell milestone**
 - Make recommendation for future composition
- Build synthesis capability within the consortium (*U Texas*)
 - Characterize
 - Supply the consortium

BATTERY500 CONSORTIUM CHOSE HIGH Ni NMC

- $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ is **baseline** for the consortium
 - X-ray characterization normal and
 - less than 3% Ni/Li mixing
 - Morphology good
 - Electrochemistry acceptable



MILESTONE: 2017 YEAR END GOAL ACHIEVED



- **300 Wh/kg Li/NMC622 pouch cell** with >100 stable cycles has been demonstrated. (project #: **bat369**)
- 313 Wh/kg Li-S pouch cell has been demonstrated but cycling is challenging. (project#: bat361)

APPROACH: QUESTIONS TO BE ADDRESSED AND ACCOMPLISHMENTS

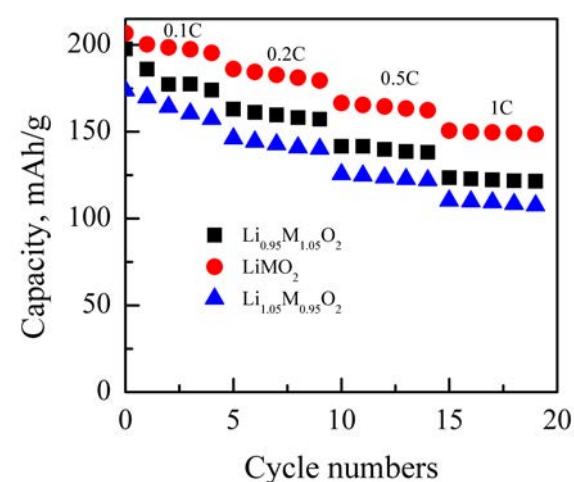
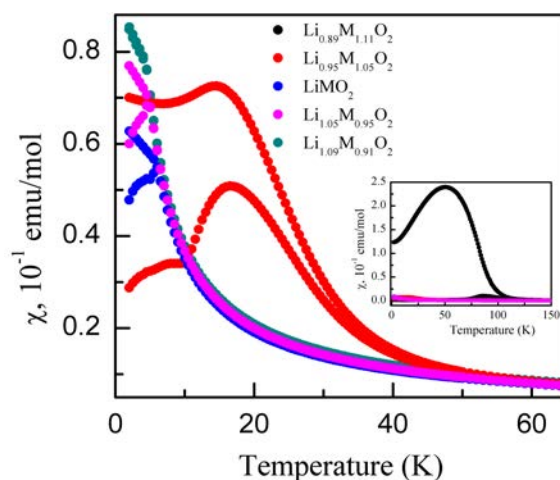
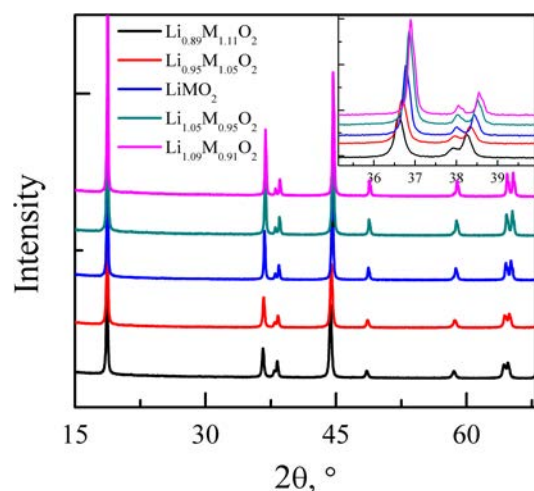
- **Evaluate Commercially available High Ni NMC:**
 - Understand 622 and 811 materials.
 - Structure, electrochemistry, morphology, ordering etc.
- **Synthesize materials in-house:**
 - Primary/secondary particle size, morphology, size distribution
- **Address several key challenges:**
 - What is the optimum composition, including Li content?
 - Are 622 and 811 truly single phase for all x values, Li_xNMC ?
 - What is fundamentally different between 811 and NCA?
 - What is the role of Al; bulk vs surface?
 - BASF says 811 must be doped and coated; Umicore says not stable longterm
 - What are the degradation mechanisms for 622 and 811?
 - Extend from know-how on 333, 442, 532 and NCA
 - Can coatings ameliorate?
 - Are gradient materials technically and cost effective?
 - What is the optimum material/morphology for thick electrodes?
- **Advanced characterization are critical**

NMC 622 CAN ACCOMMODATE RANGE OF Li

- $\text{Li}_{1+y}[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}]_{1-y}\text{O}_2$ can accommodate wide range of lithium
 - Highest capacity obtained for $\text{Li}:\text{M} = 1:1$
- 811 much less tolerant (impurity phases formed when $[\text{Li}] \neq [\text{M}]$)

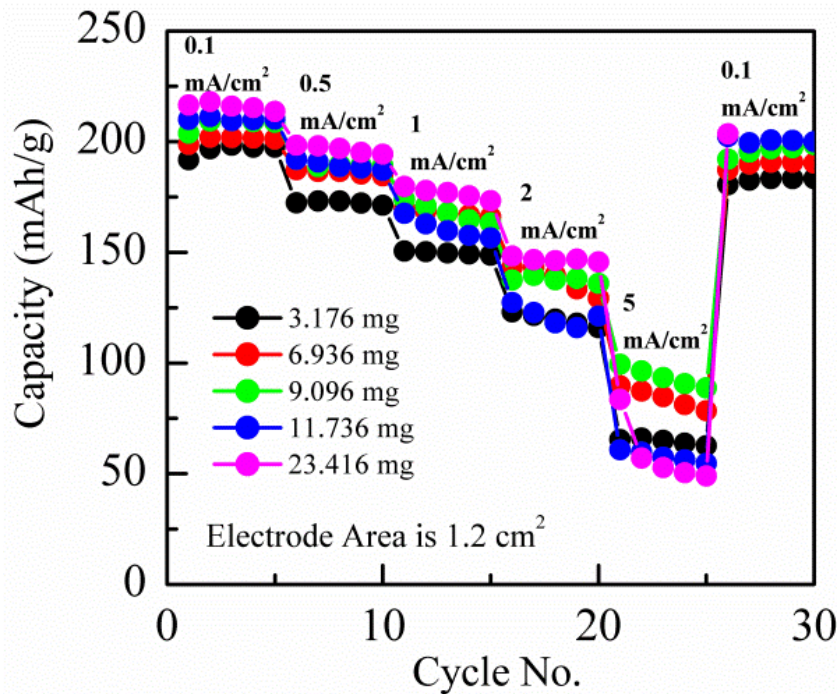
Table 1: Summary of the XRD refinement and magnetic property results for $\text{Li}_{1+y}(\text{622})_{1-y}\text{O}_2$.

| Li content | a, Å | c, Å | c/3a | Li/Ni mixing | C(emu K/mol) | Θ (K) | μ_{exp} , μB | μ_{theor} , μB |
|---|-------|--------|-------|--------------|--------------|--------------|------------------------------------|--------------------------------------|
| $\text{Li}_{0.89}\text{M}_{1.11}\text{O}_2$ | 2.878 | 14.242 | 1.650 | 8 % | 0.54 | -62 | 2.71 | 2.74 |
| $\text{Li}_{0.95}\text{M}_{1.05}\text{O}_2$ | 2.871 | 14.221 | 1.651 | 4 % | 0.675 | -43 | 2.49 | 2.57 |
| LiMO_2 | 2.863 | 14.199 | 1.653 | 2 % | 0.72 | -39 | 2.46 | 2.41 |
| $\text{Li}_{1.05}\text{M}_{0.95}\text{O}_2$ | 2.857 | 14.188 | 1.655 | - | 0.65 | -27 | 2.37 | 2.24 |
| $\text{Li}_{1.09}\text{M}_{0.91}\text{O}_2$ | 2.83 | 14.177 | 1.657 | - | 0.67 | -32 | 2.15 | 2.15 |

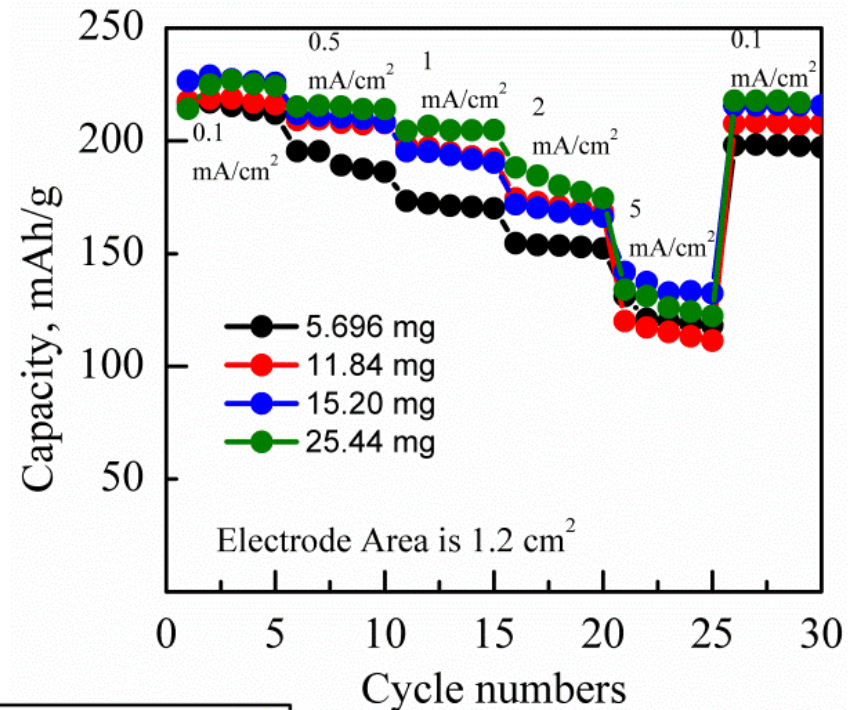


EFFECT OF LOADING ON RATE CAPABILITY:

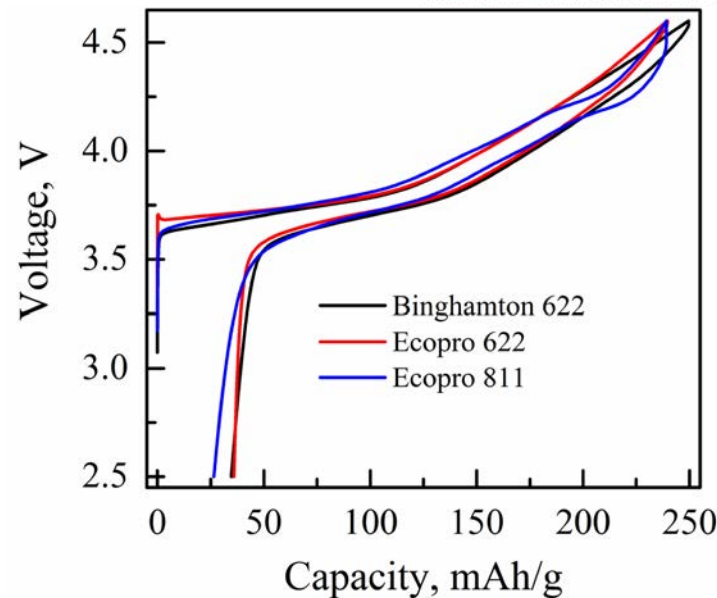
811 > 622 (BU 1 MILESTONES 2018 Q1 & Q2)



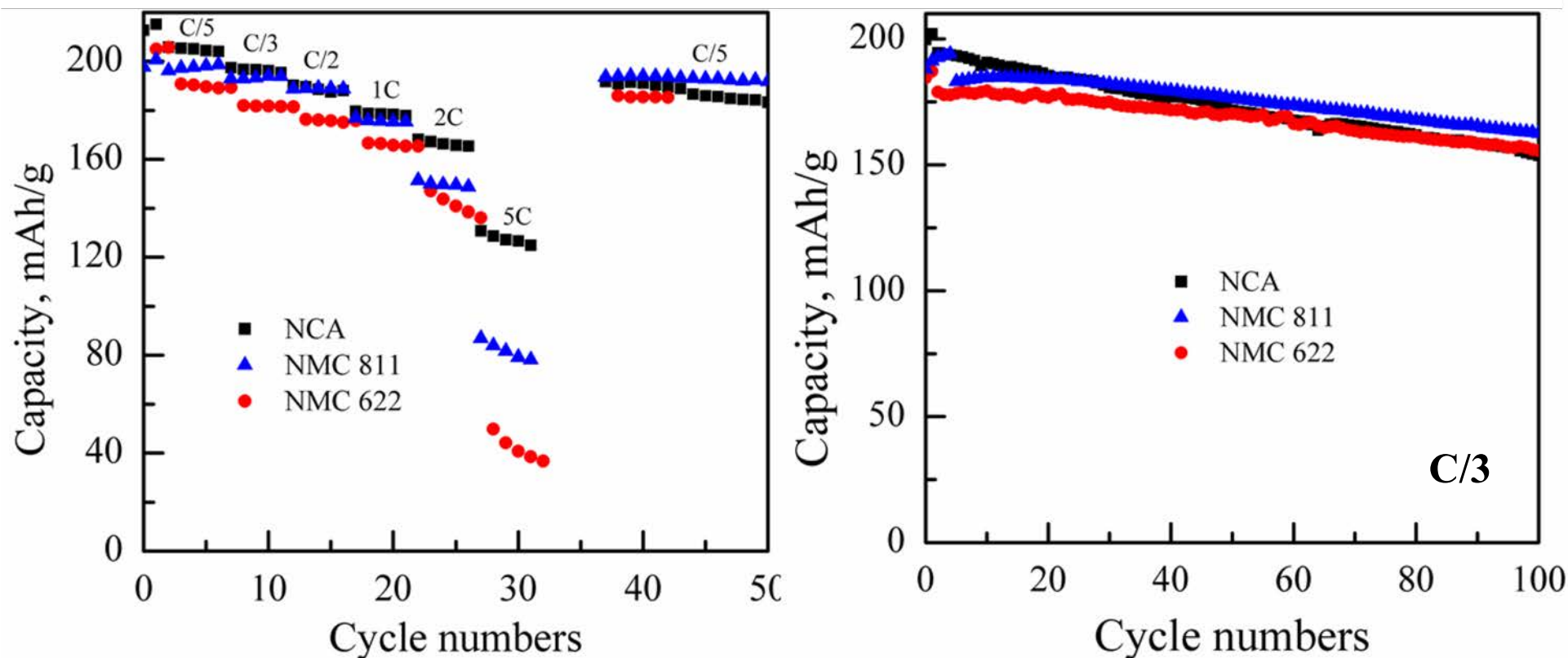
622 811



- Cycling 2.5 to 4.6 V
- Initial cycle



RATE CAPABILITY OF NCA, NMC 811 and 622

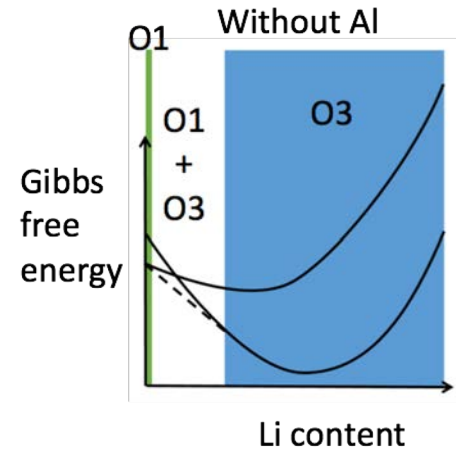


- 811 shows highest capacity
- 811 and 622 show better capacity retention than NCA
- NCA shows highest rate capability

LEARNINGS FROM NECCES NCA STUDY

• Aluminum

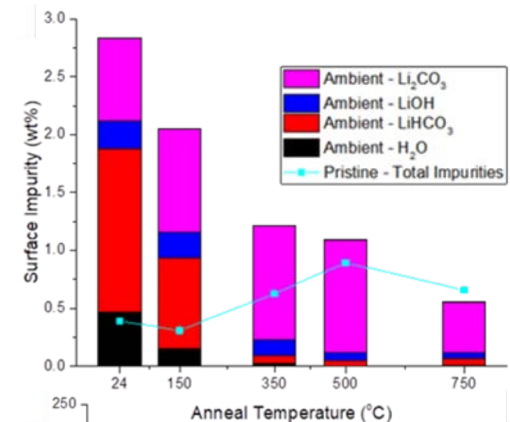
- Evenly distributed in bulk of material
 - No surface enrichment
- Al minimizes formation of O1 phase at high voltages
 - Single solid solution up to 5 V
 - Stabilizes structure, should reduce degradation
- **Learning: Al desirable for high Ni cathodes**



Radin et al AEM 2017

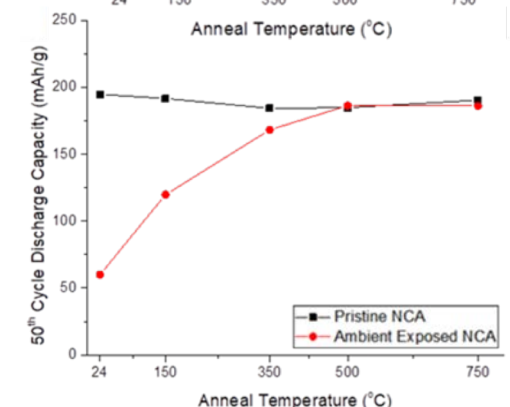
• Air Instability of NCA

- In moist air, a LiHCO_3 film is formed on the surface
 - Very detrimental to cycling capacity
- In dry air, a Li_2CO_3 film is formed on the surface
 - Decomposed at high charging voltages
- **Learning: high Ni must be protected from air**



• Extended cycling leads to cracking of particles

- Mechanical stress needs minimizing
 - Keep lattice expansion to a minimum
 - Ni: 6 $\Delta c = 2.6\%$; 8 = 3.7%; 9 = 5.6% (charging to 4.5 V)
- **Learning: Possibly limit Ni to ≤ 0.8**



Amatucci et al, JECS, 164 (2017) A3727

BASELINE 622 vs 811 (cf NCA): PROS AND CONS

➤ 622:

- + Higher thermal stability
- + Lower cost than 333

➤ 811:

- + Higher rate capability
- + More tolerant of high loadings
- ? Does it gas like NCA?
- Instability in air
- Higher than 0.8 Ni leads to larger lattice expansion, then degradation issues

➤ NCA

- + Highest rate capability
- + Most studied
- Maybe gassing issue, so needs hard case
- Unstable in moist air

BU and KEYSTONE 1 MILESTONE 2018 Q2

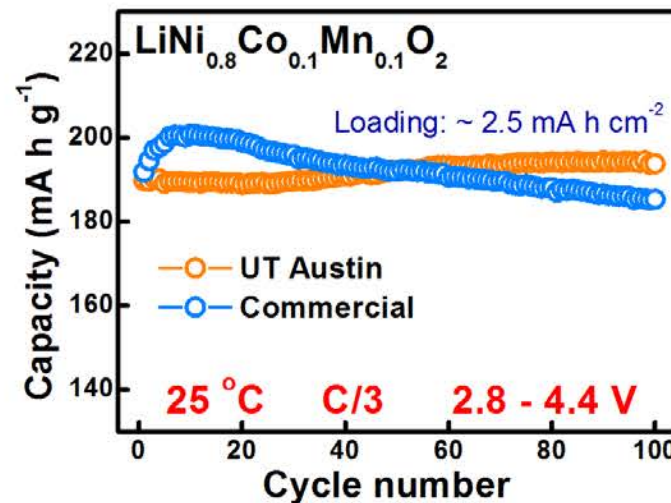
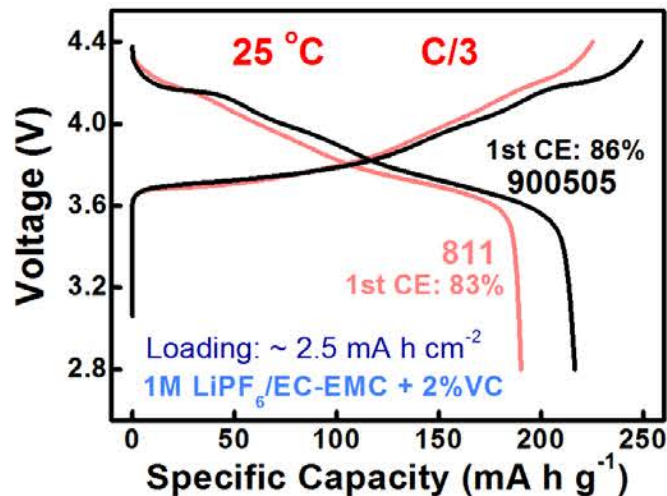
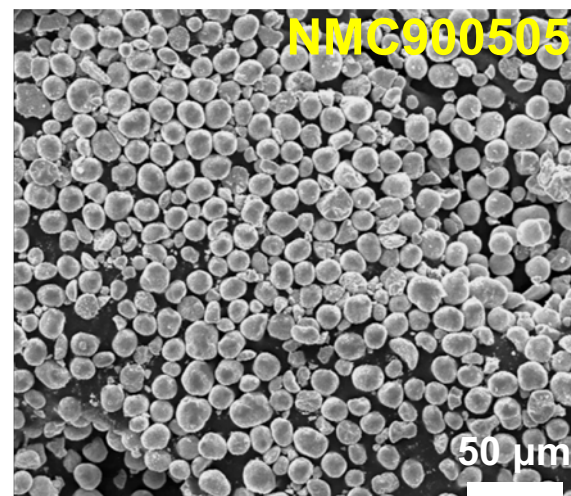
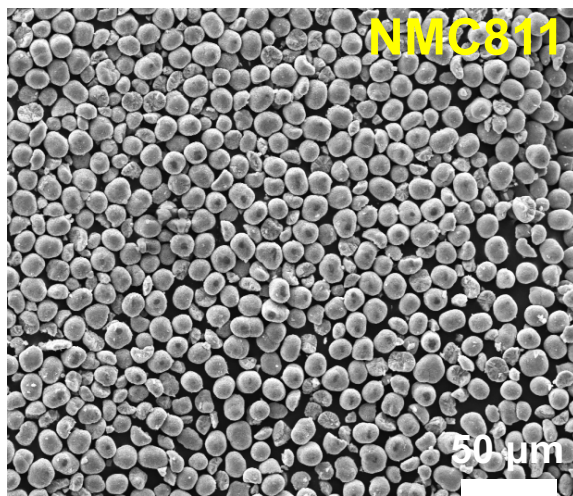
- **Milestone**
 - Recommend with Keystone 1 team the preferred NMC composition where $\text{Ni} \geq 0.7$, based on experimental and modeling studies
- **Recommendation: NMC 811 as 2018/2019 Battery 500 Cathode, as**
 - NMC 811 has higher capacity for a given charging voltage
 - NMC 811 has higher power capability
 - NMC 811 maintains capacity at high loadings better than 622
 - NMC 811 is lower cost/kWh, because of less cobalt and higher ED



NMCA

SCALED-UP SYNTHESIS OF HIGH-NICKEL NMC

KEYSTONE 1 MILESTONE 2018 Q1



In-house NMC 811 and NMC 900505 demonstrate high capacity

RESPONSE TO 2017 REVIEWERS' COMMENTS

No presentation given in 2017.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- **National Laboratories**

- PNNL, INL and BNL
 - Pouch cell studies
 - Experimental input to system modeling
 - Synchrotron: Ex-situ and operando synchrotron X-ray diffraction,
 - Neutron diffraction



- **Academia**

- UC San Diego, UT Austin and U. Washington:
 - Ni-rich NMC synthesis and characterization, doping/coating, in-situ XRD
 - Experimental input to UW modeling



- **Industry**

- Working through NYBEST and NAATBaat to disseminate information

REMAINING CHALLENGES AND BARRIERS

- **The Safety Trade-off: Energy vs Thermal Stability**
 - Increasing Ni content increases capacity
 - Increasing Ni content decreases thermal stability
 - Increasing Ni content increases capacity fade
- **Capacity Improvement**
 - Need to extract > 220 Ah/kg to achieve 500 Wh/kg cells
- **Capacity Retention**
 - The surface must be stabilized against reaction with the electrolyte
 - Metal dissolution must be eliminated
 - Cracking and other mechanical degradation must be minimized
- **Thicker Electrodes needed to decrease inactive weight**
 - Will need improved ionic conductivity in the LiMO_2
 - Will need enhanced electrode electronic conductivity

PROPOSED FUTURE WORK – KEYSTONE 1

- **Determine attributes of NCA vs 811, e.g.**
 - Gassing
 - Thermal stability (DSC et al)
 - Capacity fading
- **Evaluate options for increasing conductivity**
 - Ionic and electronic
- **Evaluate options for improving Capacity Retention**
 - Are gradient materials a possible approach?
 - Are such materials incompatible with Al doping?
 - Will they increase dissolution of Mn?
 - Determine role of doping in the lattice and/or surface coatings
- **Provide technical support to Keystone 2 and 3**

SUMMARY

- **Baseline 622 NMC Material**
 - Well characterized
 - Optimum capacity for Li:M = 1:1
 - In-house and commercial material behave the same
 - Achieved 300 Wh/kg 1st year goal
- **Recommended NMC 811 as 2018/2019 Battery 500 Cathode**
 - Higher capacity for a given charging voltage than 622
 - Al likely to be used as stabilizer
 - Achieved over 70 cycles
 - U. Texas have synthesized kg quantities
- **Comparison of NMC with NCA**
 - Al homogenizes composition
 - NCA sensitive to traces of moisture
- **Likely optimum compound is NMCA**

TECHNICAL BACK-UP SLIDES

Technical Back-Up Slides

TECHNICAL BACK-UP SLIDES

None